

APPLICATION FOR UNITED STATES PATENT

IN SITU CATALYST REGENERATION ACTIVATION PROCESS

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Figure 1. The effect of the number of trials on the number of correct responses. The number of correct responses was significantly higher than the number of incorrect responses in all cases. Error bars represent the standard error of the mean.

1. *Journal of the American Medical Association*, 2000; 284: 2689-2694.

Journal of Management Studies, 19(1), 67-80.

(AS) NO $\mathcal{N}(\mathbf{I})$ holds

IN SITU CATALYST REGENERATION ACTIVATION PROCESS

FIELD OF THE INVENTION

5 [0001] The present invention relates to an *in situ* method of regenerating catalysts used in Hydrocarbon Synthesis Catalytic (HCS) processes. Specifically, the present invention provides a means and process for *in situ* catalyst regeneration in which no "on-site" catalyst activation vessel is required
10 and in which the catalyst can be activated in a Fischer-Tropsch reactor. More specifically, the present invention provides a means and process for supported bi-metallic cobalt catalyst regeneration without interrupting the hydrocarbon synthesis continuous slurry process flow scheme and without the need for any additional catalyst activation vessels.

BACKGROUND OF THE INVENTION

15 [0002] The preparation of hydrocarbons from a mixture of hydrogen and carbon monoxide at elevated temperature and pressure in the presence of a catalyst is referred to in the literature as the Fischer-Tropsch hydrocarbon synthesis (HCS). Depending on the catalyst and conditions, the hydrocarbons may range from oxygenated compounds such as methanol and higher molecular weight alcohols, to high molecular weight paraffins which are waxy solids at room temperature. The process also makes, generally in lesser amounts, alkenes,
20 organic acids, ketones, aldehydes and esters. The synthesis is conducted in a fixed or fluidized catalyst bed reactor or in a three phase slurry reactor.

25 [0003] Hydrocarbon synthesis catalysts are well known and a typical Fischer-Tropsch hydrocarbon synthesis catalyst will comprise, for example, catalytically

effective amounts of one or more Group VIII metal catalytic components such as Fe, Ni, Co, Rh, and Ru. Preferably the catalyst comprises a supported catalyst, wherein the one or more support components of the catalyst will comprise an inorganic refractory metal oxide. The metal oxide support component is preferably one which is difficult to reduce, such an oxide of one or more metals of Groups III, IV, V, VI, and VII.

[0004] Typical support components include one or more of alumina, silica, and amorphous and crystalline aluminosilicates, such as zeolites. Particularly preferred support components are the Group IVB metal oxides, especially those having a surface area of $100 \text{ m}^2/\text{g}$ or less and even $70 \text{ m}^2/\text{g}$ or less. These support components may, in turn, be supported on one or more support materials. Titania, and particularly the rutile form of titania, is a preferred support component, especially when the catalyst contains a cobalt catalytic component. Titania is a useful component, particularly when employing a slurry hydrocarbon synthesis process, in which higher molecular weight, primarily paraffinic liquid hydrocarbon products are desired.

[0005] In some cases in which the catalyst comprises catalytically effective amounts of Co, it will also comprise one or more components or compounds of members selected from the transition metal groups VIIa or VIII of the Periodic Table (as defined in F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th Ed., Wiley, New York, 1980) as a promoter. Group VIII Nobel metals are particularly suitable. Also, rhenium, ruthenium, platinum and palladium are especially preferred. A combination of Co and Ru or Co and Re is often preferred. Useful catalysts and their preparation are known and illustrative, but nonlimiting examples may be found, for example, in U. S. patents 4,086,262,

4,492,774; 4,568,663; 4,663,305; 4,542,122; 4,621,072 and 5,545,674 and are incorporated by reference herein.

[0006] As these techniques demonstrate, after its initial formation, the catalyst undergoes a high-temperature oxidation process. Before the catalyst will properly operate in a HCS environment, it must be "activated" by reducing the oxidized catalytic metals to their metallic state. However, once activated, the catalysts are usually highly pyrophoric. Therefore commercially, most catalysts are sold after their first high-temperature oxidation, but before activation. As used herein, these newly formed, oxidized but not yet reduced catalysts are referred to as "fresh" catalyst.

[0007] The HCS catalyst may be used in either a fixed bed, fluid bed or slurry hydrocarbon synthesis processes for forming hydrocarbons from a synthesis gas comprising a mixture of H_2 and CO. These processes are well known and documented in the literature. In all of these processes, the synthesis gas is contacted with a suitable Fischer-Tropsch type of hydrocarbon synthesis catalyst, at reaction conditions effective for the H_2 and CO in the gas to react and form hydrocarbons. Depending on the process, the catalyst and synthesis reaction variables, some of these hydrocarbons will be liquid, some solid (e.g., wax) and some gas at standard room temperature conditions of temperature and pressure of 25 °C and one atmosphere, particularly if a catalyst having a catalytic cobalt component is used. In a fluidized bed hydrocarbon synthesis process, all of the products are vapor or gas at the reaction conditions. In fixed bed and slurry processes, the reaction products will comprise hydrocarbons which are both liquid and vapor at the reaction conditions.

[0008] Slurry hydrocarbon synthesis processes are sometimes preferred because of their superior heat transfer characteristics for the strongly exothermic synthesis reaction and because they are able to produce relatively high molecular weight, paraffinic hydrocarbons when using a cobalt catalyst. In a slurry hydrocarbon synthesis process, a synthesis gas comprising a mixture of H_2 and CO is bubbled up as a third phase through a slurry in a reactor which comprises a particulate Fischer-Tropsch type hydrocarbon synthesis catalyst dispersed and suspended in a slurry liquid comprising hydrocarbon products of the synthesis reaction which are liquid at the reaction conditions. The mole ratio of the hydrogen to the carbon monoxide in the synthesis gas may broadly range from about 0.5 to 4, but is more typically within the range of from about 0.7 to 2.75 and preferably from about 0.7 to 2.5.

[0009] The stoichiometric mole ratio for a Fischer-Tropsch hydrocarbon synthesis reaction is approx. 2.0, but it can be increased to obtain the amount of hydrogen desired from the synthesis gas for other than the hydrocarbon synthesis reaction. In a supported cobalt-catalyzed slurry hydrocarbon synthesis process, the mole ratio of the H_2 to CO is typically about 2.1-4. Reaction conditions effective for the various hydrocarbon synthesis processes will vary somewhat depending on the type of process, catalyst composition and desired products. Typical conditions effective to form hydrocarbons comprising mostly C_{2-} paraffins, (e.g., C_{5-} - C_{200}) and preferably C_{1-} paraffins in a slurry process employing a catalyst comprising a supported cobalt component include, for example, temperatures, pressures and gas hourly space velocities in the range of from about 150-320 $^{\circ}C$, 5.5-42.0 bar and 100-40,000 $V_{H_2}/V_{cat} \cdot hr$ (expressed as standard volumes of the gaseous CO and H_2 mixture @ 0 $^{\circ}C$, 1 atm) per hour per volume of catalyst, respectively. These conditions nominally apply to the other processes as well.

[0010] Hydrocarbons produced by a hydrocarbon synthesis process according to the practice of the invention are typically upgraded to more valuable products, by subjecting all or a portion of the C₅₊ hydrocarbons to fractionation and or conversion. By conversion is meant one or more operations in which the molecular structure of at least a portion of the hydrocarbon is changed and includes both noncatalytic processing (e.g., steam cracking), and catalytic processing (e.g., catalytic cracking) in which a fraction is contacted with a suitable catalyst. If hydrogen is present as a reactant, such process steps are typically referred to as hydroconversion and include, for example, hydroisomerization, hydrocracking, hydrodewaxing, hydrorefining and the more severe hydrorefining referred to as hydrotreating, all conducted at conditions well known in the literature for hydroconversion of hydrocarbon feeds, including hydrocarbon feeds rich in paraffins. Illustrative, but nonlimiting examples of more valuable products formed by conversion include one or more of a synthetic crude oil, liquid fuel, olefins, solvents, lubricating, industrial or medicinal oil, waxy hydrocarbons, nitrogen and oxygen containing compounds, and the like. Liquid fuel includes one or more of motor gasoline, diesel fuel, jet fuel, and kerosene, while lubricating oil includes, for example, automotive, jet, turbine and metal working oils. Industrial oil includes well drilling fluids, agricultural oils, heat transfer fluids and the like.

[0011] HCS catalysts deactivate over time at process conditions. Many short-term catalyst deactivation processes, believed to be caused by cobalt surface oxidation, coking, or exposure to some inhibitors and poisons, such as HCN, NH₃, or oxygenates may be reversed in a process known as rejuvenation. Rejuvenation is effected by contacting the deactivated catalyst with a reducing agent, preferably hydrogen. The activity of the HCS catalyst in the reactive slurry is intermittently or continuously rejuvenated by contacting the slurry with

hydrogen or a hydrogen containing gas to form a catalyst rejuvenated slurry either in-situ in the HCS reactor or in an external rejuvenation vessel, as is disclosed, for example, in U.S. patents 5,260,239, 5,268,344, 5,288,673 and 5,283,216.

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[0012] Long-term catalyst deactivation is not corrected by rejuvenation. Long-term deactivation may be corrected by a far more severe process known as regeneration. Currently, regeneration of HCS catalysts occurs outside of the HCS process. U.S. Patent 4,670,414 teaches an *ex situ* regeneration scheme which requires at least two external regeneration vessels following carefully controlled temperature and pressure programs.

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[0013] Likewise, EP 0 533 288 B1 teaches an *ex situ* regeneration scheme requiring at least four separate staged processes: the removal of the catalyst and process fluids from the process reactor, filtration or other necessary treatments to remove process reactants and products, reducing the catalyst in a hydrogen atmosphere, transferring the catalyst to a second vessel to expose it to a hydrothermal or oxidative regeneration process, transfer the catalyst to a third vessel, a catalyst activation vessel (CAV), for high temperature reduction, re-introducing the re-activated, regenerated catalyst back into the process reactor, and finally, restarting the HCS process.

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[0014] At a minimum, all current HCS catalyst regeneration processes require cessation of the HCS process removal of the catalyst to a separate regeneration vessel, transfer to a second separate reactivation (reduction) vessel before re-introduction to the HCS process. These configurations also require a means to safely transport the highly pyrophoric regenerated and reduced catalyst between the reduction vessel and the HCS reactor.

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SUMMARY OF THE INVENTION

5 [0015] The present invention provides a means and a process for activation of regenerated HCS catalysts in an *in situ* HCS process. The HCS reactor of the process of the current invention applies some form of catalyst rejuvenation means, one non-limiting form of such is described in U.S. patent 5,268,344. Specifically the present invention relates to a on-going slurry HCS process utilizing a supported Cobalt bimetallic catalyst, which allows for continuous or
10 semi-continuous removal of the catalyst to a regeneration vessel, which catalyst, once regenerated, is reactivated by directly re-introducing the regenerated catalyst in its oxidized form into the ongoing HCS process, thus requiring no separate "on site" catalyst activation vessel.

15 [0016] The invention provides for the continuous or semi-continuous, *in situ* regeneration of HCS catalysts. The method comprises periodic or continuous removal of catalyst from an operating HCS reactor to a regeneration vessel. In the regeneration vessel, the catalyst is then exposed to a regenerative environment such as a high temperature (300-500 °C) oxidative treatment. Finally, the
20 catalyst is returned to the operating HCS reactor also containing catalyst rejuvenation means allowing reduction to occur at HCS process temperatures which completes the catalyst regeneration.

BRIEF DESCRIPTION OF THE DRAWINGS

25 [0017] Figure 1 schematically illustrates a schematic cross-section of the process vessels for the regeneration of spent catalyst or activation of pre-activated passivated fresh catalyst.

[0018] Figure 2 demonstrates the late-run relative activity of a "fresh" catalyst activated in a high-temperature reduction.

[0019] Figure 3 demonstrates the relative catalytic activity of a fresh late-run catalyst reduced in a low-temperature environment

[0020] Figure 4 demonstrates the effect on catalyst activity of subsequent low-temperature reductions after a "fresh" catalyst has undergone one high-temperature reduction.

DETAILED DESCRIPTION

[0021] With respect to the hydrocarbon synthesis, fixed bed, fluid bed and slurry hydrocarbon synthesis (HCS) processes for forming hydrocarbons from a syngas comprising a mixture of H_2 and CO are well known and documented in the literature. In all of these processes the syngas is reacted in the presence of a suitable Fischer-Tropsch hydrocarbon synthesis catalyst, at reaction conditions effective to form hydrocarbons. Some of these hydrocarbons will be liquid, some solid (e.g., wax) and some gas at ambient temperature conditions and pressure (25 °C and one atmosphere), particularly if a catalyst having a catalytic cobalt component is used.

[0022] Slurry HCS processes are often preferred because of their superior heat and mass transfer characteristics for the strongly exothermic synthesis reaction and because they are able to produce relatively high molecular weight, paraffinic hydrocarbons when using a cobalt catalyst. In a slurry HCS process a syngas comprising a mixture of H_2 and CO is bubbled up as a third phase through a slurry in a reactor which comprises a particulate Fischer-Tropsch type

hydrocarbon synthesis catalyst dispersed and suspended in a slurry liquid comprising hydrocarbon products of the synthesis reaction which are liquid at the reaction conditions

8 [0023] In the cobalt-catalyzed slurry HCS process, the mole ratio of the hydrogen to the carbon monoxide may broadly range from about 0.5 to 4, but is more typically within the range of from about 0.7 to 2.75 and preferably from about 0.7 to 2.5. The stoichiometric mole ratio for a slurry Fischer-Tropsch HCS process is approximately 2:1:1, but in the practice of the present invention
10 it may be increased to obtain the amount of hydrogen desired from the syngas for other than the HCS reaction.

[0024] Slurry HCS process conditions vary somewhat depending on the catalyst and desired products. Typical conditions effective to form hydrocarbons
15 comprising mostly C₅+ paraffins, (e.g., C₅–C₂₀₀) and preferably C₇+ paraffins, in a slurry HCS process employing a catalyst comprising a supported cobalt component include, for example, temperatures, pressures and hourly gas space velocities in the range of from about 150–320°C, 5.5–42.0 bar and 100–40,000 V/hr/V, expressed as standard volumes of the gaseous CO and H₂ mixture (0°C, 1 atm) per hour per volume of catalyst, respectively
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[0025] Figure 1 details one possible embodiment of the process for the *in situ* reactivation of a regenerated catalyst. Regenerated, but not yet re-activated, catalyst (15) may be introduced into an operating HCS reactor (1). Any
25 combination of a fresh, activated catalyst, a pre-activated passivated catalyst or a short-term or a long-term deactivated catalyst may already be present in the HCS reactor (1). The HCS reactor (1) receives syngas through the inlet line (3) and releases liquid hydrocarbons through the outlet line (4) and gaseous hydrocarbon

and unreacted syngas through the offgas line (2). The HCS reactor (1) should employ at least one catalyst rejuvenation unit (14), which is fed with a catalyst rejuvenating fluid (12). Catalyst within the HCS reactor (1) may freely enter and exit the catalyst rejuvenation unit (14).

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[0026] Catalyst is removed from the HCS reactor (1) through the slipstream line (5). This line feeds to filtration unit (6) which is fed with a stripping fluid (7) if necessary. Spent stripping fluid and stripped byproducts are removed from the filtration unit (6) through the filtration unit outlet line (8). The filtered catalyst proceeds to the regeneration unit (9) which is fed a regenerative fluid (10). The regenerated catalyst is returned to the HCS reactor (1) through the catalyst return line (11) wherein it is reactivated.

[0027] Many embodiments of the present invention are possible. The applicant provides numerous embodiments, none of which are meant to limit the invention in any way. In one embodiment, the filtration unit (6) is an H_2 stripping unit. The regeneration unit (9) employs oxidative treatments at above 300 °C. In another embodiment, the slipstream line (5) and the catalyst return line (11) are the same line.

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[0028] In another embodiment, the invention comprises the steps of

1. removing a portion of a hydrocarbon synthesis catalyst from an operating HCS process which may contain catalyst rejuvenation means,
2. removing the reactants and products of the process from the catalyst,
3. exposing the catalyst to a regeneration environment, and

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- 4 reintroducing the catalyst into the HCS process environment for catalyst reduction

5 [0029] It is well known that standard catalyst rejuvenation techniques successfully reverse short-term deactivation mechanisms such as fouling, coking and carbon formation. Standard means of catalyst rejuvenation are accomplished by exposing the catalyst to any metal reducing substance; in the HCS process of the present invention it is preferably accomplished by exposing the catalyst to a
10 full or partial H_2 stream in an area of lessened HCS process activity. Rejuvenation, however, does not reverse long-term deactivation mechanisms. One significant advantage of rejuvenation is that it may be employed *in situ* at reactor conditions, thus allowing for extended catalyst use in a continuous process environment.

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[0030] Catalyst regeneration to reverse long-term deactivation requires conditions not found in a standard HCS catalytic process environment. Because of this, catalyst regeneration has not been successfully integrated into a continuous or semi-continuous *in situ* HCS catalytic process environment. The
20 present invention's discovery of low temperature reduction following the catalytic regeneration process allows for continuous or semi-continuous catalytic process.

[0031] In the past, catalyst would be regenerated by removing the catalyst
25 from the process reactor, transferring it to a first vessel for high temperature (300-500 °C) oxidation, then transferring it to a second vessel, a Catalyst Activation Vessel, for high temperature (375 °C) reduction and finally returning the catalyst to the hydrocarbon synthesis process reactor. The object of the present invention is to simplify this process by eliminating the high temperature

reduction step, thereby allowing a continuous or semi-continuous regeneration with catalyst reactivation (reduction) directly by the HCS fluids

[0032] In another embodiment, the current invention relates to a Fischer-Tropsch process using a Co-Re TiO_2 catalyst. Once activated, a spent catalyst may be oxidized and then be essentially fully reduced at the operating temperature of the Fischer-Tropsch slurry unit completing the catalyst regeneration. The catalyst need not be processed through a separate catalyst activation vessel to re-reduce it after oxidation. Instead, it may be re-reduced and fully activated in the slurry unit containing rejuvenation means. This allows for a continuous or semi-continuous process flow scheme where some of the catalyst is periodically or continuously removed from an operating HCS slurry reactor, treated in a regenerative environment and then directly returned to the operating slurry unit

[0033] The process of the present invention is further described by way of the following illustrative examples which are not intended to limit the scope of the invention in any manner whatsoever

Example 1

[0034] "Fresh" Co-Re catalyst on a TiO_2 support was activated and placed in a Fischer-Tropsch reactor. Two samples were removed: an early-run sample, which was removed a few days after the reactor was in operation, and a late-run sample which was removed very late in the run cycle. Each sample was removed to a dry box and the wax extracted with hot toluene under inert conditions

[0035] Each sample was divided into two portions. The first portion of each sample was directly transferred under inert condition into a chemisorption unit and the H_2 chemisorptions, a standard measure of catalytic activity, were measured by a dual isotherm technique. This technique is described by C.H. Bartholomew in " H_2 Adsorption on Supported Noble Metals and its Use in Determining Metal Dispersion", *Catalysis*, Vol. 11, pp. 93-126 (1994) CODEN CATADK ISSN:0140-0568, CAN 123-66509 AN 1995 536025 CAPLUS. The second portion of each sample was regenerated in a high temperature (350 °C) oxidative (air) environment, and then reduced in the presence of H_2 at 225 °C. The second portion of each sample was then transferred under inert condition into a chemisorption unit and the H_2 chemisorptions were measured by a dual isotherm technique. Table I illustrates the chemisorption results.

TABLE I

% Strong H Chemisorption values (H/Co) after reduction at 225°C.
Combined and back sorption isotherms measured at 40°C.

Sample	After Wax Extraction	After regeneration with air at 350 °C
Early-run - inertly wax extracted	3.75	4.47
Late-run - inertly wax extracted	1.61	4.12

[0036] The first column of Table I shows far higher H chemisorption values for the non-regenerated early-run catalyst as compared to non-regenerated late-run catalyst. This indicates that the early-run catalyst was rejuvenated under reduction conditions present in the 225 °C H_2 chemisorption. But, as expected, the late-run catalyst was not rejuvenated due to long-term deactivation mechanisms that are not reversed by hydrogen treatment. Fresh catalyst, measured after a 375 °C H_2 reduction and a 150 °C air oxidation have a H chemisorption value of approximately 3.7 to 4.1.

[0037] As the second column of Table 1 demonstrates, late-run catalyst activity increased significantly after regeneration by high temperature oxidation followed by low temperature reduction demonstrating that the current invention's regeneration *in situ* (low, H₂S temperature) reactivation process successfully reversed the majority of long-term deactivation effects. The oxidative regeneration followed by a low temperature H₂ treatment restores almost all (within 10%) of the catalytically active sites as are present in the fresh catalyst. Also as expected, the early-run catalyst showed small H chemisorption increases after high temperature oxidative regeneration as the majority of activity loss was due to short-term deactivation effects.

EXAMPLE 2

[0038] A "fresh" (non-activated) catalyst was reduced (activated) in a hydrogen atmosphere at high temperature conditions (1200 kPa, 400°C for 8 hours). The catalyst was then placed in a Fischer-Tropsch synthesis reactor operated at 200°C, 20-25 bar with a 2:1 H₂:CO ratio. The activity of the catalyst was determined by measuring the catalyst productivity (moles of CO converted/volume of catalyst), adjusted for differences in reaction conditions using a kinetic model similar to those found in W. D. Deckwer, "Kinetic Studies of Fischer-Tropsch Synthesis on Suspended Fe-K Catalyst - Rate Inhibition by CO₂ and H₂O", Ind. Eng. Chem. Process Dev., Vol 25, pp. 643-649 (1986). Relative activity levels for this catalyst are reported in Figure 2. The activity level for this "fresh", high-temperature reduced catalyst averaged slightly less than 12.0 as expected.

EXAMPLE 3

[0039] The same experiment as in Example 2 was conducted except that the initial hydrogen reduction of the "fresh" catalyst was conducted at low-
 5 temperature rejuvenation conditions (220°C, 2000kPa for 12 hours). As in example two, the catalyst was placed in a Fischer-Tropsch reactor (at the same operating conditions) and the relative activity was measured. The relative activities for this catalyst are reported in Figure 3. The relative activity for this catalyst ranged between 5.0 and 5.5. These results clearly demonstrate that a
 10 low-temperature reduction of a "fresh" catalyst did not activate the catalyst to acceptable HCS activity levels.

Example 4

15 [0040] A sample of catalyst prepared in the same manner as that in example 2 was inertly extracted from an operating Fischer-Tropsch reactor early in the reactor's run. This sample was loaded into a fixed bed reactor operating at the same Fischer-Tropsch conditions as in example 2. After approximately four days, the catalyst was stripped of wax under a H₂ flow, and then oxidized with a
 20 1% O₂ in nitrogen gas mixture at 20 atmospheres. Following this regeneration procedure, the catalyst was reduced at 200 °C for 12 hours at 20.25 bar of H₂ pressure, the Fischer-Tropsch reaction continued. After Approximately 5.5 days, a similar wax stripping treatment was performed, the catalyst was regenerated in the same manner, but was re-reduced at 400 °C for 8 hours under 12 atmospheres
 25 of H₂ pressure. The relative activity values are shown in Figure 4.

[0041] Figure 4 shows that the activity starts at a relative activity unit of approximately 9 and, as expected, slowly decreases with time. After a regeneration at 350 °C and a reduction at 220 °C, the activity increases again to

approximately 10%. A comparison between the effectiveness of the later regeneration process using low temperature re-reduction and high temperature re-reduction (at 400 °C) demonstrates that the activity does not change relative to the reduction temperature once the catalyst is reduced and oxidized at least once

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[0042] This demonstrates that following a catalyst's first high-temperature reduction, any subsequent reduction may be a low temperature reduction and still restore the catalyst to full activity. This invention eliminates the need for transferring the catalyst to a separate reduction vessel for activation after
10 regeneration. Further, this invention allows for a continuous, in situ regeneration re-activation process, eliminating the previous requirement to interrupt the HCS process.